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Natural gas

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1. Introduction

This chapter contains a description of background of natural gas: what exactly natural gas is?, how it is formed and how it is found in nature; history of natural gas: a brief history and development of modern natural gas; resources: how much abundance, where to find and what is the composition of natural gas; Uses: application and the important of energy source; natural gas versus environment: emission from the combustion of natural gas; natural gas technology: role of technology in the evolution of the natural gas industry; Purification of crude natural gas: various technologies used to convert sour to sweet natural gas; synthesis of artificial natural gas: methanation reaction.

2. Background of Natural Gas

A mixture of gaseous hydrocarbons occurring in reservoirs of porous rock (commonly sand or sandstone) capped by impervious strata. It is often associated with petroleum, with which it has a common origin in the decomposition of organic matter in sedimentary deposits. Natural gas consists largely of methane (CH_4) and ethane (C_2H_6), with also propane (C_3H_8) and butane (C_4H_{10})(separated for bottled gas), some higher alkanes (C_5H_{12} and above) (used for gasoline), nitrogen (N_2) , oxygen (O_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and sometimes valuable helium (He). It is used as an industrial and domestic fuel, and also to make carbon-black and chemical synthesis. Natural gas is transported by large pipelines or (as a liquid) in refrigerated tankers. Natural gas is combustible mixture of hydrocarbon gases, and when burned it gives off a great deal of energy. We require energy constantly, to heat our homes, cook our food, and generate our electricity . Unlike other fossil fuels, however, natural gas is clean burning and emits lower levels of potentially harmful byproducts into the air. It is this need for energy that has elevated natural gas to such a level of importance in our society, and in our lives.

Natural Gas is a vital component of the world's supply of energy. It is one of the cleanest, safest, and most useful of all energy sources. Despite its importance, however, there are many misconceptions about natural gas. For instance, the word 'gas' itself has a variety of different uses, and meanings. When we fuel our car, we put 'gas' in it. However, the gasoline that goes into your vehicle, while a fossil fuel itself, is very different from natural gas. The 'gas' in the common barbecue is actually propane, which, while closely associated and commonly found in natural gas, is not really natural gas itself. While commonly

grouped in with other fossil fuels and sources of energy, there are many characteristics of natural gas that make it unique. Below is a bit of background information about natural gas, what exactly it is, how it is formed, and how it is found in nature

2.1 History of Natural Gas

Naturally occurring natural gas was discovered and identified in America as early as 1626, when French explorers discovered natives igniting gases that were seeping into and around Lake Erie. The American natural gas industry got its beginnings in this area. In 1859, Colonel Edwin Drake (a former railroad conductor who adopted the title 'Colonel' to impress the townspeople) dug the first well. Drake hit oil and natural gas at 69 feet below the surface of the earth.

Fig. 1. A Reconstruction of 'Colonel' Drake's First Well in Titusville, Pa (Source: API)

Most in the industry characterize this well (Fig.1) as the beginning of the natural gas industry in America. A two-inch diameter pipeline was built, running 5 and ½ miles from the well to the village of Titusville, Pennsylvania. The construction of this pipeline proved that natural gas could be brought safely and relatively easy from its underground source to be used for practical purposes.

In 1821, the first well specifically intended to obtain natural gas was dug in Fredonia, New York, by William Hart. After noticing gas bubbles rising to the surface of a creek, Hart dug a 27 foot well to try and obtain a larger flow of gas to the surface. Hart is regarded by many as the 'father of natural gas' in America. Expanding on Hart's work, the Fredonia Gas Light Company was eventually formed, becoming the first American natural gas company.

In 1885, Robert Bunsen invented what is now known as the Bunsen burner (Fig.2). He managed to create a device that mixed natural gas with air in the right proportions, creating a flame that could be safely used for cooking and heating. The invention of the Bunsen burner opened up new opportunities for the use of natural gas in America, and throughout

the world. The invention of temperature-regulating thermostatic devices allowed for better use of the heating potential of natural gas, allowing the temperature of the flame to be adjusted and monitored.

Fig. 2. A Typical Bunsen Burner (Source:DOE)

Without any way to transport it effectively, natural gas discovered pre-world war II was usually just allowed to vent into the atmosphere, or burnt, when found alongside coal and oil, or simply left in the ground when found alone.

One of the first lengthy pipelines was constructed in 1891. This pipeline was 120 miles long, and carried natural gas from wells in central Indiana to the city of Chicago. However, this early pipeline was very rudimentary, and did not transport natural gas efficiently. It wasn't until the 1920's that any significant effort was put into building a pipeline infrastructure. After World War II welding techniques, pipe rolling, and metallurgical advances allowed for the construction of reliable pipelines. This led to a post-war pipeline construction boom lasting well into the 60's, creating thousands of miles of pipeline in America.

Once the transportation of natural gas was possible, new uses for natural gas were discovered. These included using natural gas to heat homes and operate appliances such as water heaters and oven ranges. Industry began to use natural gas in manufacturing and processing plants. Also, natural gas was used to heat boilers used to generate electricity. The transportation infrastructure made natural gas easier to obtain, and as a result expanded its uses.

2.2 How Natural Gas is Formed

Millions of years ago, the remains of plants and animals decayed and built up in thick layers. This decayed matter from plants and animals is called organic material –a compound that capable of decay or sometime refers as a compound consists mainly carbon. Over time,

the mud and soil changed to rock, covered the organic material and trapped it beneath the rock. Pressure and heat changed some of this organic material into coal, some into oil (petroleum), and some into natural gas – tiny bubbles of odorless gas. The main ingredient in natural gas is methane, a gas (or compound) composed of one carbon atom and four hydrogen atoms, CH_4. It is colorless, shapeless, and odorless in its pure form.

In some places, gas escapes from small gaps in the microscopic plants and animals living in the ocean rocks into the air; then, if there is enough activation energy from lightning or a fire, it burns. When people first saw the flames, they experimented with them and learned they could use them for heat and light. The formation of natural gas can be explained starting with microscopic plants and animals living in the ocean.

The process began in amillions of years ago, when microscopic plants and animals living in the ocean absorbed energy from the sun, which was stored as carbon molecules in their bodies. When they died, they sank to the bottom of the sea. Over millions of years, layer after layer of sediment and other plants and bacteria were formed.

As they became buried ever deeper, heat and pressure began to rise. The amount of pressure and the degree of heat, along with the type of biomass (biological materials derived from living organisms), determined if the material became oil or natural gas. More heat produced lighter oil. At higher heat or biomass made predominantly of plant material produced natural gas.

After oil and natural gas were formed, they tended to migrate through tiny pores in the surrounding rock. Some oil and natural gas migrated all the way to the surface and escaped. Other oil and natural gas deposits migrated until they were caught under impermeable layers of rock or clay where they were trapped. These trapped deposits are where we find oil and natural gas wells today where drilling process was conducted to obtain the gas.

In a modern technology, machines called "digesters" is used to turn today's organic material (plants, animal wastes, etc.) into synthetic natural gas (SNG). This replaces waiting for thousands of years for the gas to form naturally and could overcome the depletion of natural resources. The conventional route for SNG production is based on gasification of biomass to produce synthesis gas and then the subsequent methanation of the synthesis gas turn it to synthesis natural gas. Woody biomass contain 49.0% carbon and 5.7% hydrogen that can be converted to 76.8% methane, CH_4.

2.3 How Natural Gas is Obtained

Now imagine how to obtain the invisible treasure? That's the challenge face by geologist when exploring for natural gas. Sometimes there are clues on the earth's surface. An oil seeps is a possible sign of natural gas below, since oil and gas are sometimes found together. Geologists also have sensitive machines that can "sniff" surface soil and air for small amounts of natural gas that may have leaked from below ground.

The search for natural gas begins with geologists who locate the types of rock that are known to contain gas and oil deposits. Today their tools include seismic surveys that are used to find the right places to drill wells. Seismic surveys use echoes from a vibration source at the Earth's surface (usually a vibrating pad under a truck built for this purpose) to collect information about the rocks beneath. They send sound waves into the ground and measure how fast the waves bounce back. This tells them how hard and how thick the different rock layers are underground. The data is fed into a computer, which draws a

picture of the rock layers. This picture is called a seismogram. Sometimes, it is necessary to use small amounts of dynamite to provide the vibration that is needed.
The next task are taken by scientists and engineers who explore a chosen area by studying rock samples from the earth and taking measurements. If the site seems promising, drilling begins. Some of these areas are on land but many are offshore, deep in the ocean. Once the gas is found, it flows up through the well to the surface of the ground and into large pipelines. Some of the gases that are produced along with methane, such as butane and propane, are separated and the other sour gases such as carbon dioxide and hydrogen sulfide are cleaned at a gas processing plant (normally called as sweetening process). The by-products, once removed, are used in a number of ways. For example, propane and butane can be used for cooking gas.
Because natural gas is colorless, odorless and tasteless, mercaptan (a sulfur-containing organic compound with the general formula RSH where R is any radical, especially ethyl mercaptan, C_2H_5SH) is added before distribution, to give it a distinct unpleasant odor (like that of rotten eggs). This serves as a safety device by allowing it to be detected in the atmosphere, in cases where leaks occur.
Most of the natural gas consumed in the United States is produced in the United States. Some is imported from Canada and shipped to the United States in pipelines. Increasingly natural gas is also being shipped to the United States as liquefied natural gas (LNG).

2.4 How Natural Gas is Stored and Delivered

Natural gas is normally produced far away from the consumption regions, therefore they requires an extensive and elaborate transportation system to reach its point of use. The transportation system for natural gas consists of a complex network of pipeline, designed to quickly and efficiently transport natural gas from the origin to areas of high natural gas demand. Transportation of natural gas is closely linked with its storage since the demand of the gas is depend on the season.
Since natural gas demand is greater in the winter, gas is stored along the way in large underground storage systems, such as old oil and gas wells or caverns formed in old salt beds in western country. The gas remains there until it is added back into the pipeline when people begin to use more gas, such as in the winter to heat homes. In Malaysia, and other tropical country, gas is supplied throughout the year, therefore it was storage in a large tank in the processing plant, either in Bintulu, Sarawak, or at Kertih, Terengganu.
Three major types of pipeline available along the transportation route, the gathering system, the interstate pipeline and the distribution system. The gathering system consists of low pressure, low diameter pipelines that transport raw natural gas from the wellhead to the processing plant. In Malaysia, the natural gas is transported from oil rig offshore to the processing plant at Petronas Gas Berhad at Kertih, Terengganu, and Bintulu LNG Tanker, Sarawak. Since Malaysia natural gas and other producing country contain high sulfur and carbon dioxide (sour gaseous) it must used specialized sour gas gathering pipe. Natural wet gas from the wellhead contain high percentage of water therefore it will react with sour gaseous to form acids, which are extremely corrosive and dangerous, thus its transportation from the wellhead to the sweetening plant must be done carefully. The topic will be discussed in depth in the treatment and processing of natural gas.
Pipeline can be classified as interstate or intrastate either it carries natural gas across the state boundary (interstate) or within a particular state (intrastate). Natural gas pipelines are

subject to regulatory oversight, which in many ways determines the manner in which pipeline companies must operate. When the gas gets to the communities where it will be used (usually through large pipelines), the gas is measured as it flows into smaller pipelines called mains. Very small lines, called services, connect to the mains and go directly to homes or buildings where it will be used. This method is used by rich country such as in the United State, Canada or European country, such as United Kingdom, France etc.

The used of pipeline for natural gas delivery is costly, therefore some countries prefer to use trucks for inland delivery. Using this method the natural gas should be liquefied to minimize the size of the tanker truck. In certain country, the natural gas is transported by trucks tankers to the end users. For example in Malaysia the natural gas was transported as Liquefied Natural Gas (LNG) using tanker trucks to different state in peninsular of Malaysia and in East Malaysia. The gas was supplied by Petronas Gas Berhad, at Kertih, Terengganu while in east Malaysia, Sabah and Sarawak, the gas was supplied by Bintulu Plant. The natural is exported by large ships equipped with several domed tanks.

When chilled to very cold temperatures, approximately -260°F, natural gas changes into a liquid and can be stored in this form. Because it takes up only 1/600th of the space that it would in its gaseous state, Liquefied natural gas (LNG) can be loaded onto tankers (large ships with several domed tanks) and moved across the ocean to deliver gas to other countries. When this LNG is received in the United States, it can be shipped by truck to be held in large chilled tanks close to users or turned back into gas to add to pipelines. The whole process to obtain the natural gas to the end user can be simplified by the diagram shown in Fig. 3.

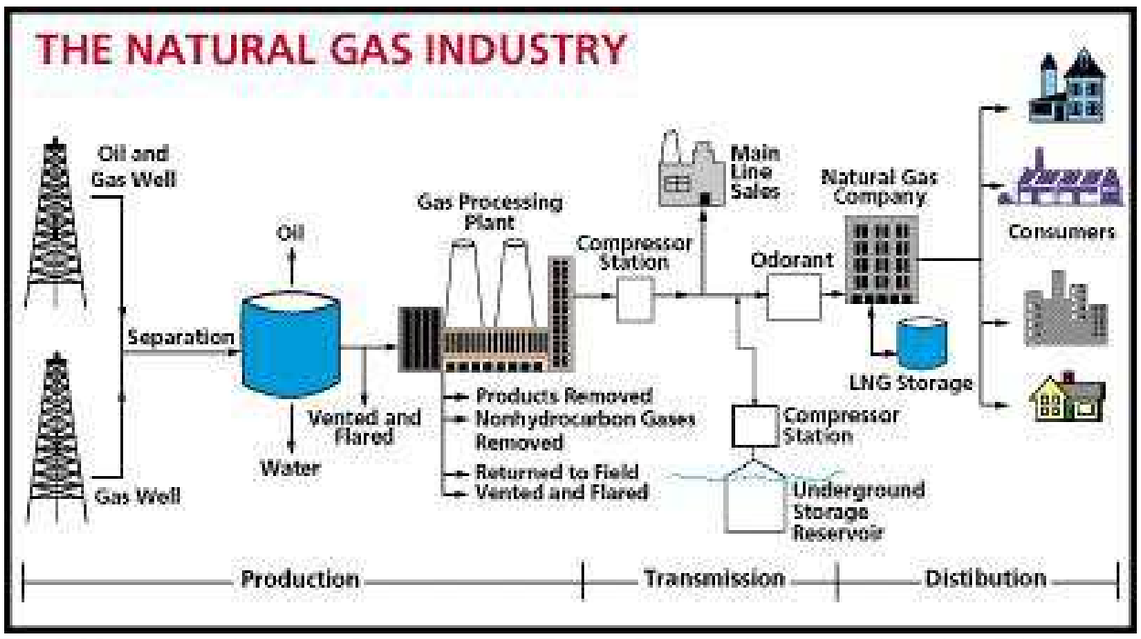

Fig. 3. Natural gas industry. Image (source: Energy Information Administration, DOE)

2.5 What is the Composition of Natural Gas

Natural gas, in itself, might be considered a very uninteresting gas - it is colorless, shapeless, and odorless in its pure form. Quite uninteresting - except that natural gas is combustible,

and when burned it gives off a great deal of energy. Unlike other fossil fuels, however, natural gas is clean burning and emits lower levels of potentially harmful byproducts into the air. We require energy constantly, to heat our homes, cook our food, and generate our electricity. It is this need for energy that has elevated natural gas to such a level of importance in our society, and in our lives.

Natural gas is a combustible mixture of hydrocarbon gases. While natural gas is formed primarily of methane, it can also include ethane, propane, butane and pentane. The composition of natural gas can vary widely, but below is a chart outlining the typical makeup of natural gas before it is refined.

Chemical Name	**Chemical Formula**	**Percentage (%)**
Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Rare gases	A, He, Ne, Xe	trace

Table 1. Typical composition of Natural Gas

In its purest form, such as the natural gas that is delivered to your home, it is almost pure methane. Methane is a molecule made up of one carbon atom and four hydrogen atoms, and is referred to as CH_4. Malaysia producing sour natural gas. Before purification process, Malaysia's natural gas is consists of several gaseous and impurities. The chemical composition of Malaysia natural gas before it is being refined is shown in Table 2.

Chemical Name	**Chemical Formula**	**Percentage (%)**
Methane	CH_4	40-50%
Ethane	C_2H_6	5-10%
Propane	C_3H_8	1-5%
Carbon Dioxide	CO_2	20-3-%
Hydrogen sulphide	H_2S	0-1%

Table 2. Chemical composition in crude natural gas provided by Bergading Platform offshore of Terengganu, Malaysia.

2.6 How Much Natural Gas is there

There is an abundance of natural gas in North America, but it is a non-renewable resource, the formation of which takes thousands and possibly millions of years. Therefore, understanding the availability of our supply of natural gas is important as we increase our use of this fossil fuel. This section will provide a framework for understanding just how much natural gas there is in the ground available for our use, as well as links to the most recent statistics concerning the available supply of natural gas.

As natural gas is essentially irreplaceable (at least with current technology), it is important to have an idea of how much natural gas is left in the ground for us to use. However, this becomes complicated by the fact that no one really knows exactly how much natural gas exists until it is extracted. Measuring natural gas in the ground is no easy job, and it involves a great deal of inference and estimation. With new technologies, these estimates are becoming more and more reliable; however, they are still subject to revision.

Natural Gas Resource Category	As of January 1, 2007(Trillion Cubic Feet)
Nonassociated Gas	
Undiscovered	**373.20**
Onshore	113.61
Offshore	259.59
Inferred Reserves	**220.14**
Onshore	171.05
Offshore	49.09
Unconventional Gas Recovery	**644.92**
Tight Gas	309.58
Shale Gas	267.26
Coalbed Methane	68.09
Associated-Dissolved Gas	**128.69**
Total Lower 48 Unproved	**1366.96**
Alaska	**169.43**
Total U.S. Unproved	**1536.38**
Proved Reserves	**211.09**
TOTAL NATURAL GAS	**1747.47**

Table 3. Natural Gas Technically Recoverable Resources (Source: Energy Information Administration - Annual Energy Outlook 2009)

A common misconception about natural gas is that we are running out, and quickly. However, this couldn't be further from the truth. Many people believe that price spikes, seen in the 1970's, and more recently in the winter of 2000, indicate that we are running out of natural gas. The two aforementioned periods of high prices were not caused by waning natural gas resources - rather, there were other forces at work in the marketplace. In fact,

there is a vast amount of natural gas estimated to still be in the ground. In order to understand exactly what these estimates mean, and their importance, it is useful first to learn a bit of industry terminology for the different types of estimates.
The EIA provides classification system for natural gas resources. Unconventional natural gas reservoirs are also extremely important to the nation's supply of natural gas.
Below are three estimates of natural gas reserves in the United States. The first (Table 3), compiled by the Energy Information Administration (EIA), estimates that there are 1,747.47 Tcf of technically recoverable natural gas in the United States. This includes undiscovered, unproved, and unconventional natural gas. As seen from the table, proved reserves make up a very small proportion of the total recoverable natural gas resources in the U.S.
The following table includes an estimate of natural gas resources compiled by the National Petroleum Council (NPC) in 1999 in its report Natural Gas - Meeting the Challenges of the Nation's Growing Natural Gas Demand. This estimate places U.S. natural gas resources higher than the EIA, at 1,779 Tcf remaining. It is important to note that different methodologies and systems of classification are used in various estimates that are completed. There is no single way that every industry player quantifies estimates of natural gas. Therefore, it is important to delve into the assumptions and methodology behind each study to gain a complete understanding of the estimate itself.

	1992 NPC Study	**1999 NPC Study**
	As of Jan 1, 1991	As of Jan 1, 1998
Lower 48 Resources		
Proved Reserves	160	157
Assessed Additional Resources	1135	1309
Old Fields (Reserve Appreciation)	236	305
New Fields	493	633
Nonconventional	406	371
Total Remaining Resources	**1295**	**1466**
Alaskan Resources		
Proved Reserves	9	10
Assessed Additonal Resources	171	303
Old Fields (Reserve Appreciation)	30	32
New Fields	84	214
Nonconventional	57	57
Total Remaining Resources	**180**	**313**
Total U.S. Remaining Resources	**1475**	**1779**

Table 4. U.S. Natural Gas Resources (Trillion Cubic Feet) (Source: National Petroleum Council - Meeting the Challenges of the Nation's Growing Natural Gas Demand, 2007)

Below (Table 5) is a third estimate completed by the Potential Gas Committee. This estimate places total U.S. natural gas resources at just over 1,836 Tcf. This estimate classifies natural gas resources into three categories: probable resources, possible resources, and speculative resources, which are added together to reach a total potential resource estimate. Only this total is shown below.

	Total Potential Resource
Traditional Resources	
Lower 48 States	
Total Lower 48	**1479.6**
Alaska	
Onshore	94.432
Offshore	99.366
Total Alaska	**193.831**
Total Traditional	**1,673.4**
Coalbed Methane	**163.0**
Total United States	**1,836.4**

Table 5. Potential Natural Gas Resources of the U.S. (Trillion Cubic Feet) (Source: Potential Gas Committee - Potential Supply of Natural Gas in the United States, 2009)

There are a myriad of different industry participants that formulate their own estimates regarding natural gas supplies, such as production companies, independent geologists, the government, and environmental groups, to name a few. While this leads to a wealth of information, it also leads to a number of difficulties. Each estimate is based on a different set of assumptions, completed with different tools, and even referred to with different language. It is thus difficult to get a definitive answer to the question of how much natural gas exists. In addition, since these are all essentially educated guesses as to the amount of natural gas in the earth, there are constant revisions being made. New technology, combined with increased knowledge of particular areas and reservoirs mean that these estimates are in a constant state of flux. Further complicating the scenario is the fact that there are no universally accepted definitions for the terms that are used differently by geologists, engineers, accountants, and others.

Natural gas has been discovered on all continents except Antarctica. World natural gas reserves total approximately 150 trillion cu m (5.3 quadrillion cu ft). The world's largest natural gas reserves, totaling, 50 trillion cu m (1.9 quadrillion cu ft) are located in Russia. The second-largest reserves, 48 trillion cu m (1.7 quadrillion cu ft), are found in the Middle East. Vast deposits are also located in other parts of Asia, in Africa, and in

Australia. Natural gas reserves in the United States total 5 trillion cu m (177 trillion cu ft). In Asia-Oceania, natural gas reserves total 12.6 trillion cu m (Table 6). Malaysia has the 14th largest gas reserves as at January 2008. As at January 2008, Malaysia's gas reserves stood at 88.0 trillion standard cubic feet (tscf) or 14.67 billion barrels of oil equivalent, approximately three times the size of crude oil reserves of 5.46 billion barrels.

	Proven reserves (Tm^3)	**Annual production (Gm^3)**	**Reserve to product (years)**
Australia	2.5	34.5	72.5
China	1.5	32.6	46.0
India	0.8	28.4	28.2
Indonesia	2.6	70.6	36.8
Malaysia	2.1	50.3	41.8
Others	3.1	85.3	36.3
Total	**12.6**	**301.7**	**41.8**

Table 6. Proven reserves and Annual production, Asia-Oceania. (Taken from BP Statistical Review, 2003)

Most of this gas reserves are located at offshore Peninsular Malaysia, Sarawak and Sabah. The Malaysian natural gas reserves are as shown in Figure 4 [4].

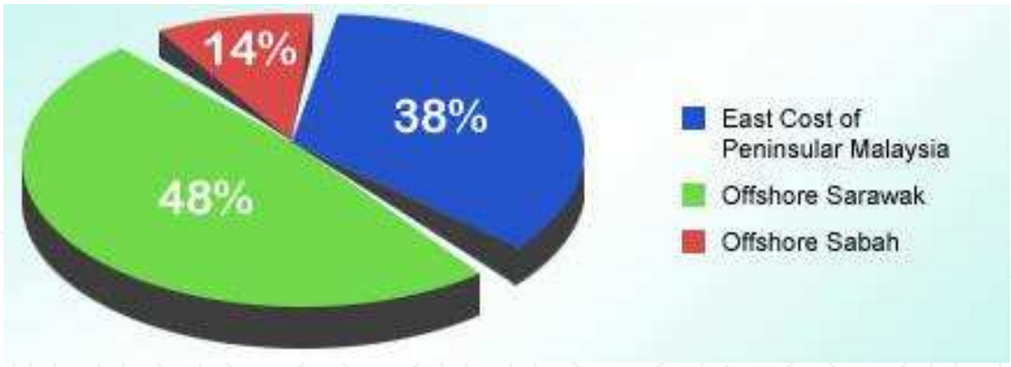

Fig. 4. Malaysian Natural Gas Reserve (Taken from Oil and Gas Exploration and Production-Reserves, Costs, Contract, 2004)

Currently, Malaysia is a net exporter of natural gas and is the third largest exporter after Algeria and Indonesia. In 2001, the country exported 49.7% of its natural gas production to the Republic of Korea and Taiwan under long-term contracts. The other 50.3% of Malaysia natural gas was delivered to the gas processing plants.

2.7 Uses of Natural Gas

For hundreds of years, natural gas has been known as a very useful substance. The Chinese discovered a very long time ago that the energy in natural gas could be harnessed, and used to heat water. In the early days of the natural gas industry, the gas was mainly used to light streetlamps, and the occasional house. However, with much improved distribution channels and technological advancements, natural gas is being used in ways never thought possible.

There are so many different applications for this fossil fuel that it is hard to provide an exhaustive list of everything it is used for. And no doubt, new uses are being discovered all the time. Natural gas has many applications, commercially, in your home, in industry, and even in the transportation sector! While the uses described here are not exhaustive, they may help to show just how many things natural gas can do.

According to the Energy Information Administration, total energy (Fig. 5) from natural gas accounts for 23% of total energy consumed in the developing countries, making it a vital component of the nation's energy supply.

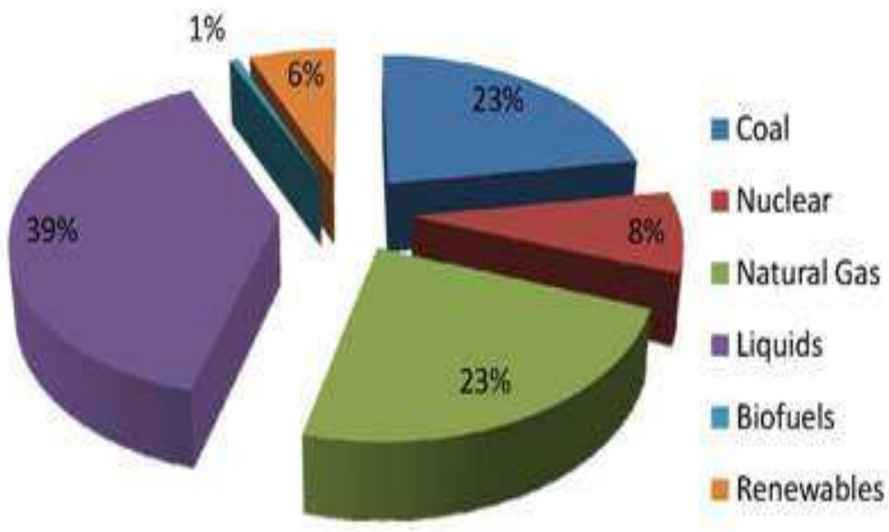

Fig. 5. Total Energy Consumed in the U.S. - 2007 (Source: EIA - Annual Energy Outlook 2009)

Natural gas is used across all sectors, in varying amounts. The pie chart below (Fig. 6) gives an idea of the proportion of natural gas use per sector. The residential sector accounts for the greatest proportion of natural gas use in the most of the developing countries, with the residential sector consuming the greatest quantity of natural gas.

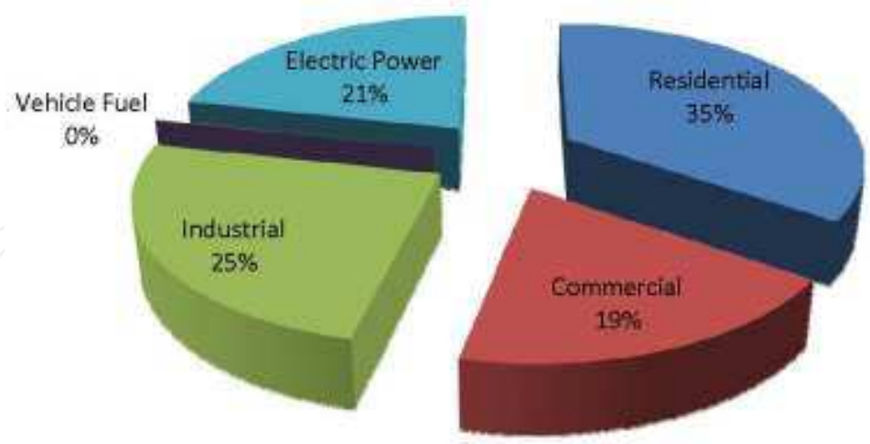

Fig. 6. Natural Gas Use By Sector (Source: EIA - Annual Energy Outlook 2009)

Commercial uses of natural gas are very similar to electric power uses. The commercial sector includes public and private enterprises, like office buildings, schools, churches, hotels, restaurants, and government buildings. The main uses of natural gas in this sector include space heating, water heating, and cooling. For restaurants and other establishments that require cooking facilities, natural gas is a popular choice to fulfill these needs.
According to the Energy Information Administration (EIA), as of the year 2003, the commercial sector consumes about 6,523 trillion Btu's of energy a year (aside from electrical system losses), most of which is required for space heating, lighting, and cooling. Of this 6,523 trillion Btu, about 2,100 trillion Btu (or 32.2%) are supplied by natural gas.

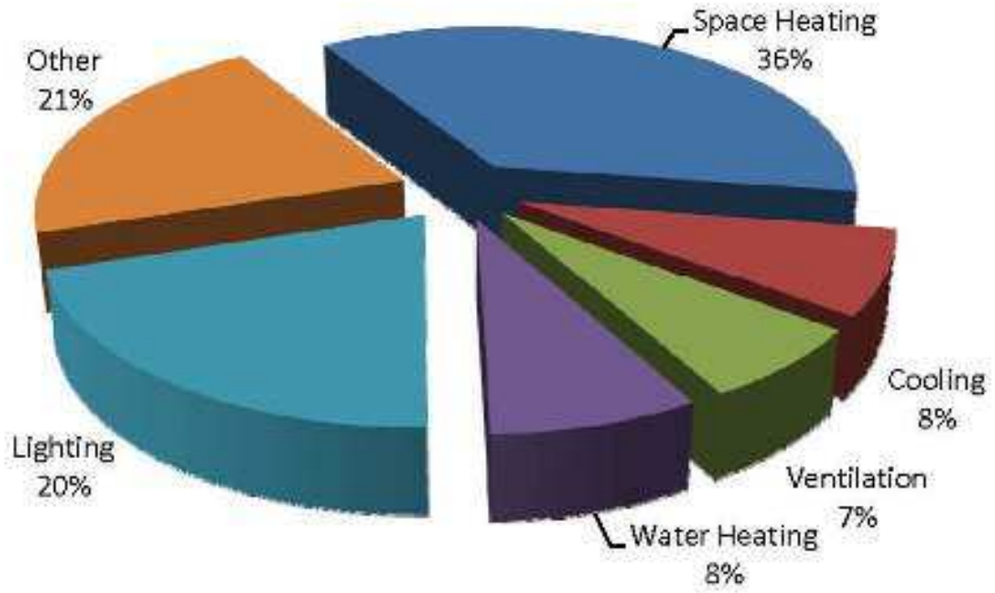

Fig. 7. Commercial Energy Use (Source: EIA Major Fuel Consumption by End Use, 2003.)

Natural gas space and water heating for commercial buildings is very similar to that found in residential houses. Natural gas is an extremely efficient, economical fuel for heating in all types of commercial buildings. Although space and water heating account for a great deal of natural gas use in commercial settings, non-space heating applications are expected to account for the majority of growth in natural gas use in the commercial sector. Cooling and cooking represent two major growth areas for the use of natural gas in commercial settings.
Natural gas currently accounts for 13 percent of energy used in commercial cooling, but this percentage is expected to increase due to technological innovations in commercial natural gas cooling techniques. There are three types of natural gas driven cooling processes. Engine driven chillers use a natural gas engine, instead of an electric motor, to drive a compressor. With these systems, waste heat from the gas engine can be used for heating applications, increasing energy efficiency. The second category of natural gas cooling devices consist of what are called absorption chillers, which provide cool air by evaporating a refrigerant like water or ammonia. These absorption chillers are best suited to cool large commercial buildings, like office towers and shopping malls. The third type of commercial cooling system consists of gas-based desiccant systems (Fig. 8). These systems cool by reducing humidity in the air. Cooling this dry air requires much less energy than it would to cool humid air.

Fig. 8. A Desiccant Unit Atop the Park Hyatt Hotel, Washington D.C. (Source: National Renewable Energy Laboratory, DOE)

Another area of growth in commercial natural gas use is in the food service industry. Natural gas is an excellent choice for commercial cooking requirements, as it is a flexible energy source in being able to supply the food service industry with appliances that can cook food in many different ways. Natural gas is also an economical, efficient choice for large commercial food preparation establishments. New developments such as Nontraditional Restaurant Systems, which provide compact, multifunctional natural gas

appliances for smaller sized food outlets such as those found in shopping malls and airports, are expanding the commercial use of natural gas. These types of systems can integrate a gas-fired fryer, griddle, oven, hot and cold storage areas, and multiple venting options in a relatively small space - providing the ease and efficiency of natural gas cooking while being compact enough to serve small kiosk type establishments.

In addition to traditional uses of natural gas for space heating, cooling, cooking and water heating, a number of technological advancements have allowed natural gas to be used to increase energy efficiency in commercial settings. Many buildings, because of their high electricity needs, have on-site generators that produce their own electricity. Natural gas powered reciprocating engines, turbines, and fuel cells are all used in commercial settings to generate electricity. These types of 'distributed generation' units offer commercial environments more independence from power disruption, high-quality consistent electricity, and control over their own energy supply.

Another technological innovation brought about is combined heating and power and combined cooling, heating and power systems, which are used in commercial settings to increase energy efficiency. These are integrated systems that are able to use energy that is normally lost as heat. For example, heat that is released from natural gas powered electricity generators can be harnessed to run space or water heaters, or commercial boilers. Using this normally wasted energy can dramatically improve energy efficiency.

Natural gas fired electric generation, and natural gas powered industrial applications, offer a variety of environmental benefits and environmentally friendly uses, including:

- Fewer Emissions - combustion of natural gas, used in the generation of electricity, industrial boilers, and other applications, emits lower levels of NO_x, CO_2, and particulate emissions, and virtually no SO_2 and mercury emissions. Fig. 9 shows a picture of emissions from Industrial Smokestacks (Source: EPA). Natural gas can be used in place of, or in addition to, other fossil fuels, including coal, oil, or petroleum coke, which emit significantly higher levels of these pollutants.
- Reduced Sludge - coal fired power plants and industrial boilers that use scrubbers to reduce SO_2 emissions levels generate thousands of tons of harmful sludge. Combustion of natural gas emits extremely low levels of SO_2, eliminating the need for scrubbers, and reducing the amounts of sludge associated with power plants and industrial processes.
- Reburning - This process involves injecting natural gas into coal or oil fired boilers. The addition of natural gas to the fuel mix can result in NO_x emission reductions of 50 to 70 percent, and SO_2 emission reductions of 20 to 25 percent.
- Cogeneration - the production and use of both heat and electricity can increase the energy efficiency of electric generation systems and industrial boilers, which translates to requiring the combustion of less fuel and the emission of fewer pollutants. Natural gas is the preferred choice for new cogeneration applications.
- Combined Cycle Generation - Combined cycle generation units generate electricity and capture normally wasted heat energy, using it to generate more electricity. Like cogeneration applications, this increases energy efficiency, uses less fuel, and thus produces fewer emissions. Natural gas fired combined cycle generation units can be up to 60 percent energy efficient, whereas coal and oil generation units are typically only 30 to 35 percent efficient.

- Fuel Cells - Natural gas fuel cell technologies are in development for the generation of electricity. Fuel cells are sophisticated devices that use hydrogen to generate electricity, much like a battery. No emissions are involved in the generation of electricity from fuel cells, and natural gas, being a hydrogen rich source of fuel, can be used. Although still under development, widespread use of fuel cells could in the future significantly reduce the emissions associated with the generation of electricity.
- Essentially, electric generation and industrial applications that require energy, particularly for heating, use the combustion of fossil fuels for that energy. Because of its clean burning nature, the use of natural gas wherever possible, either in conjunction with other fossil fuels, or instead of them, can help to reduce the emission of harmful pollutants.

Fig. 9. Emissions from Industrial Smokestacks (Source: EPA)

3. Purification of Natural Gas

Gas processing of acidic crude natural gas is necessary to ensure that the natural gas intended for use is clean-burning and environmentally acceptable. Natural gas used by consumers is composed almost entirely of methane but natural gas that emerges from the reservoir at the wellhead contains many components that need to be extracted. Although, the processing of natural gas is less complicated rather than the processing and refining of crude oil, it is equal and necessary before it can be used by end user.

One of the most important parts of gas processing is the removal of carbon dioxide and hydrogen sulfide. The removal of acid gases (CO_2, H_2S and other sulfur components) from natural gas is often referred to as gas sweetening process. There are many acid gas treating processes available for removal of CO_2 and H_2S from natural gas. These processes include Chemical solvents, Physical solvents, Adsorption Processes Hybrid solvents and Physical separation (Membrane) (Kohl and Nielsen, 1997).

3.1 Various Technologies Used to Convert Sour to Sweet Natural Gas

According to previous research done by Hao *et al.* (2002), there are ways to upgrading the low quality natural gas with selective polymer membranes. The membrane processes were designed to reduce the concentrations of CO_2 and H_2S in the natural gas pipeline specifications. However, this technique incurs high cost and low selectivity towards toxic gas separation. This technique also needs further development because the performance of membrane depends upon the specific characteristics of flue gas composition, and the specific features of the separation (i.e. large volumetric flow rate, low pressure source, high temperature, and the relative low commodity value of H_2S and CO_2) (Rangwala, 1996).

Another method of H_2S removal and one that leaves the CO_2 in the natural gas is called the Iron Sponge process. The disadvantage of this is that it is called a batch-type function and is not easily adapted to continuous operating cycle. The Iron Sponge is simply the process of passing the sour gas through a bed of wood chips that have been impregnated with a special hydrated form of iron oxide that has a high affinity for H_2S. Regeneration of the bed incurs excessive maintenance and operating costs, making this method inconsistent with an efficient operating program. If there are any real advantages in using this process, it is fact that CO_2 remains in the gas, thereby reducing the shrinkage factor which could be significant for very large volumes with an otherwise high CO_2 content (Curry, 1981).

Chemical absorption processes with aqueous alkanolamine solutions are used for treating gas streams containing CO_2. They offer good reactivity at low cost and good flexibility in design and operation. However, depending on the composition and operating conditions of the feed gas, different amines can be selected to meet the product gas specification (Mokhatab et al., 2006). Some of the commonly used alkanolamine for absorption desulfurization are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), di-isopropanolamine (DIPA) and methyldiethanolamine (MDEA). MDEA allows the selective absorption of H_2S in the presence of CO_2 but can be use effectively to remove CO_2 from natural gas in the present of additives (Salako and Gudmundsson, 2005).

In the other hand, CO_2 can be removed from natural gas via chemical conversion techniques. Catalysts for CO_2 methanation have been extensively studied because of their application in the conversion of CO_2 gas to produce methane, which is the major component in natural gas (Wan Abu Bakar *et al.*, 2008a). Usually, the catalysts are prepared from the metal oxide because of the expensiveness of pure metal. This process can increase the purity and quality of the natural gas without wasting the undesired components but fully used them to produce high concentration of methane (Ching Kuan Yong, 2008).

3.2 Synthesis of Artificial Natural Gas: Methanation Reaction

Methane (CH_4) gas was formed from the reaction of hydrogen gas and carbon dioxide gas through methanation process by reduction reaction as in Equation 1.1 below:-

$$CO_{2\,(g)} + 4H_{2\,(g)} \rightarrow CH_{4\,(g)} + 2H_2O_{\,(l)} \quad (1.1)$$

This reaction is moderately exothermic, H^o = -165 kJ/mol. In order for this method to be effective, a suitable catalyst must be applied to promote selectively CO_2 methanation because of the main side product under this reaction also will be form (Eq 1.2), which obviously should be avoided. Thus, high selectivity of the catalyst in promoting CO_2

methanation is paramount importance. In Equation 1.2, carbon monoxide produced by this reaction can also be used to form methane by reaction with hydrogen.

$$CO_{2\,(g)} + H_{2\,(g)} \rightarrow CO_{(g)} + H_2O_{(l)} \quad (1.2)$$

$$CO_{(g)} + 3H_{2\,(g)} \rightarrow CH_{4\,(g)} + H_2O_{(l)} \quad (1.3)$$

3.2.1 Mechanism of Methanation Reaction

Mechanism of methanation reaction has been studied a long time ago. A lot of researcher agreed that methanation process involves Langmuir-Hinshelwood (LH) mechanism to support the reaction process between active species and catalyst surface.
For the simplest possible reaction, methanation process can be described as follows:

$$CO_2 + S \rightleftharpoons CO_{2(ads)} \quad (1.4)$$

$$H_2 + S \rightleftharpoons H_{2(ads)} \quad (1.5)$$

$$CO_{2(ads)} + H_{2(ads)} \rightleftharpoons CH_{4(ads)} + H_2O_{(ads)} \quad (1.6)$$

$$CH_{4(ads)} \rightleftharpoons CH_{4(desorp)} + S \quad (1.7)$$

$$H_2O_{(ads)} \rightleftharpoons H_2O_{(desorp)} + S \quad (1.8)$$

Where S = Catalyst surface; ads = adsorbed species on the catalyst surface; desorp = desorbed species from catalyst surface.

According to Equation 1.4, carbon dioxide is reacting with the catalyst surface, (S) by chemisorptions and creates an active species that adsorbed onto catalyst surface. This is followed by hydrogen compound that also react with catalyst surface by chemisorptions and adsorbed onto catalyst surface as an active species. Both active species than react each other to produce products that is methane and water. Finally, (Equation 1.7 & 1.8) both products were dissociated from the catalyst surface.

4. Catalysts Used in Methanation Reaction

Metal oxide supported catalysts have been widely used in research for investigating the CO and CO_2 methanation reaction. Depending on the metal used and the reaction conditions, a variety of products may be formed including methane. However, fewer researches on the catalyst for in-situ reactions of CO_2 methanation and H_2S desulfurization have been carried out. In fact, there is also presence of H_2S in real natural gas. Therefore, H_2S should be considered in invention of methanation catalyst, since it could cause poisoning of the nickel catalyst (Wan Abu Bakar *et al.*, 2008b). As been said by Xu *et al.* (2003), a good methanation catalyst is physically durable and reducible at temperature not more than 300°C with high performance ability and these properties should retained in the catalyst while in use with a life span up to 10 years.

4.1 Nickel Oxide Based used in Methanation Catalysts

The methanation of carbon dioxide on Ni catalysts was studied in detail by fewer researchers because of the theoretical significance and possible practical application of this reaction. The methanation activity of Ni/Al_2O_3 catalyst depended intimately on the surface chemical state of Ni and different active phases formed from the reduction of different nickel species in the oxidated states. Nickel oxides appeared in Ni/Al_2O_3 in two forms prior to reduction as "free" and "fixed oxide", and formed large and small crystallites, respectively, when reduced (Zielinski, 1982). Studied done by Rodriguez *et al.* (2001) showed that NiO catalyst has ability to gives higher catalytic activity with higher methane formation due to the malformation sites which converted to active sites on the surface of nickel oxide. This property is important as reference to construct excellent catalysts for CO_2 conversion

Previously, it was shown that nickel particles change their morphology during catalytic reactions by cluster growth processes and that part of the active clusters are lifted from the support due to carbon deposition and carbon whisker formation (Czekaj *et al.*, 2007). Early study by Douglas *et al.*, (2001) found that Ni catalysts are promising catalysts since they are active and more resistant to sulfur poisoning thus high dispersion of Ni and is expected to be used in catalytic reaction that proceeds at relatively low temperature (Takahashi *et al.*, 2007). Moreover, Inui (1996) claimed that NiO has a bimodal pore structure, which will enhance the higher activity for CO_2 methanation. A bimodal pore structure was found to be beneficial to catalyst preparation and methanation rate (Inui, 1979) which will serve as an optimum pore size for the adsorption of both the reactants. Therefore, Ni based catalyst are commonly used as catalysts in hydrogenation and hydrogenolysis reaction.

Aksoylu and Onsan (1997) reported 5.5×10^{-5} % of CH_4 was produced at 250°C over the Ni/Al_2O_3 catalyst prepared by conventional impregnation method at 350°C for 3 hours under reduction environment. They also investigated the 15%-Ni/Al_2O_3 prepared by coprecipitation method for methanation of carbon dioxide. The result achieved 30% of conversion with 99.7% selectivity towards methane at 510 K (Aksoylu *et al.*, 1996). Some previous research was only focused on conversion of CO_2 without mentioned the yielded of CH_4. Similarly to Chang *et al.* (2003) who had investigated CO_2 methanation over NiO supported on rice husk ash-Al_2O_3 and SiO_2-Al_2O_3 which had been synthesized by impregnation method and calcined at 500°C. At reaction temperature of 400°C, there were 30% conversion of CO_2 over the rice husk ash-Al_2O_3 supported catalyst, while only 5% conversion of CO_2 over the SiO_2-Al_2O_3 catalyst.

Moreover, Ni/SiO catalyst prepared by conventional impregnation method was also studied by Shi and Liu, (2009). The sample was treated by glow discharge plasma for 1 hour and followed by calcinations thermally at 500°C for 4 hours. Such prepared catalyst presents smaller metal particles (17.5 and 7.9 nm) and higher conversion of CO at 400°C around 90% for methantion reaction. However, Ni/SiO_2 catalyst prepared by a sol gel process showed better quality when compared to the Ni/SiO_2 catalyst prepared by conventional impregnation (Tomiyama *et al.*, 2003). Thus, Takahashi *et al.* (2007) investigated the bimodal pore structure of Ni/SiO_2 prepared by the sol-gel method of silicon tetraethoxide and nickel nitrate in the presence of poly(ethylene oxide) (PEO) and urea.

They found that the catalyst shows steady activity which around 30-40% without decay within the reaction period until 240 min with total flow rate of 360 cm^3/min. The performance of the catalyst influenced strongly by Ni surface area rather than the presence

of macropores. As been shown that, nickel oxide can be prepared through various methods such as wetness impregnation, co-precipitation, sol gel method, ion-exchange, adsorption, deposition-precipitation and else. These preparation methods are, however very complicated and difficult to control except for wetness impregnation method. Therefore, most of the work published has focused on the use of impregnation technique for their catalyst preparation.

Research done by Liu *et al.* (2008) on the removal of CO contained in hydrogen-rich reformed gases was conducted by selective methanation over Ni/ZrO_2 catalysts prepared by conventional wetness impregnation method. The catalyst achieved CO conversion of more than 96% and held a conversion of CO_2 under 7% at temperature range 260°C-280°C. The results showed that only methane was observed as a hydrogenated product. Furthermore, the maximum of CO_2 conversion was found by Perkas *et al.* (2009) which achieved about 80% at 350°C on the Ni/meso-ZrO_2 catalyst. Around 100% selectivity to CH_4 formation was obtained at the same reaction temperature. This catalyst was prepared by an ultrasound-assisted method and testing with gas hourly space velocity (GHSV) of 5400 h-1 at all temperatures. They also reported that none modified mesoporous Ni/ZrO_2 catalyst and with the Ni/ZrO_2 modified with Ce and Sm did not effect the conversion of CO_2. Previous work by Sominski *et al.* (2003), a Ni catalyst supported on a mesoporous yttria-stabilized-zirconia composite was successfully prepared by a sonochemical method using templating agent ofvsodium dodecyl sulfate (SDS). However, the result is not as good as the catalyst that had been obtained by Perkas *et al.*

In a research done by Rostrup-Nielsen *et al.* (2007), supported nickel catalyst containing 22 wt% Ni on a stabilized support was exposed to a synthesis gas equilibrated at 600°C and 3000kPa for more than 8000h. The CO_2 conversion is 57.87% while methane formed is 42.76%. The research showed that at 600°C, loss of active surface area proceeds via the atom migration sintering mechanism. The methanation reaction is structure sensitive and it was suggested that atomic step sites play the important role as the active sites of the reaction. High temperature methanation may play a role in manufacture of substitute natural gas (SNG). The key problem is resistance to sintering, which results in a decrease of both the metal surface area and the specific activity.

Modification of the catalyst by some appropriate additives may effect the conversion of CO_2 which then methane production. Ni catalysts were modified by alkali metal, alkaline earth metals, transition metal, noble metal or rare earth metal just to select which promoters could increase the conversion of CO_2 as well as the methane formation. The effect of cerium oxide as a promoter in supported Ni catalysts was studied by Xavier et al. (1999). They claimed that the highest activity of CeO_2 promoter for Ni/Al_2O_3 catalysts could be attributed to the electronic interactions imparted by the dopant on the active sites under reducing conditions. The testing was evaluated in a high pressure catalytic reactor consists of a stainless steel reactor of 25 mm diameter and 180 mm length which is mounted vertically inside a furnace. Methanation activity and metal dispersion was found to decrease with increasing of metal loading. It is observed that the catalyst doped with 1.5 wt% CeO_2 exhibited highest conversion of CO and CO_2 with percentage of conversion increase 3.674 moles/second, which is 86.34%. The presence of CeO_2 in impregnated $Ni/\gamma\text{-}Al_2O_3$ catalysts was associated with easier reduction of chemical interaction between nickel and alumina support hence increase its reducibility and higher nickel dispersion Zhuang *et al.* (1991). It showed a

beneficial effect by not only decreasing the carbon deposition rate but also increasing and maintaining the catalytic activity.

The study of Yoshida *et al.* (1997) in a bench scale test at ambient temperature and 350°C for carbon recycling system using Ni ferrite process was carried out in LNG power plant. The feed gas was passed at a flow rate of 10 mL/min. They found that the amount of methane formed after CO_2 decomposition was 0.22 g (conversion CO_2 of to CH_4: 77%) in the latter and 0.49 g (conversion of CO_2 to CH_4: 35%) in the former. According to their study, the methanation and carbon recycling system could also be applied to other CO_z sources such as IGCC power plant and depleted natural gas plant. Hence, pure CH_4 gas can be theoretically synthesized from CO_2 with low concentration in flue gas and H_2 gas with the minimum process energy loss, while conventional catalytic processes need an additional separation process of CH_4 gas formed.

Hashimoto *et al.* (2002) who revealed that the catalysts obtained by oxidation-reduction treatment of amorphous Ni-Zr alloys exhibited high catalytic activity with 100% selectivity formation of CH_4 at 1 atm. Around 80% of CO_2 was converted at 573 K. They found the number of surface nickel atom decreases with nickel content of catalyst, because of coagulation of surface nickel atoms leading to a decrease in dispersion of nickel atoms in the catalysts. Moreover, Habazaki *et al.* (1998) reported that over the catalysts prepared from amorphous Ni-Zr (-Sm) and Co-Zr, nickel-containing catalysts show higher activity than the Co-Zr catalyst. CO reacted preferentially with H_2 and was almost completely converted into CH_4 at or above 473 K in the CO-CO_2-H_2. The maximum conversion of carbon dioxide under the present reactant gas composition is about 35% at 575 K.

Most of the previous work used rare earth oxide as a dopant over Ni/Al_2O_3 catalysts for hydrogenation reaction. Su and Guo (1999) also reported an improvement in catalytic activity and resistance to Ni sintering of doped with rare earth oxides. The growth of Ni particles and the formation of inactive NiO and $NiAl_2O_4$ phases were suppressed by addition of rare earth oxides. The combinations of two oxides lead to creation of new systems with new physicochemical properties which may exhibit high catalytic performance as compared to a single component system (Luo *et al.,* 1997). However, the catalytic and physicochemical properties of different oxide catalysts are dependent mainly on the chemical composition, method of preparation and calcination temperatures (Selim and El-Aihsy, 1994).

Ando and Co-workers (1995) had studied on intermetallic compounds synthesized by arc-melting metal constituent in a copper crucible under 66.7 kPa argon atmosphere. The hydrogenation of carbon dioxide took place under 5 Mpa at a reaction temperature at 250°C over $LaNi_4X$. They found that the conversion of CO_2 was 93% over $LaNi_5$ and the selectivities to methane and ethane in the product were 98% and 2%, respectively. The source of activity can be attributed to the new active sites generated by decomposition of the intermetallic compounds. However, even under atmospheric pressure, 56% of CO_2 converted to CH_4 and CO with selectivities of 98% and 2%, respectively.

The promotion of lanthanide to the nickel oxide based catalyst gives positive effects which are easier reduction of oxide based, smaller particles size and larger surface area of active nickel (Zhang *et al.*, 2001). Moreover, the highly dispersed nickel crystallites is obtained over nickel catalyst containing of lanthanide promoter (Rivas *et al.*, 2008). Furthermore, the methanation of carbon dioxide over Ni-incorporated MCM-41 catalyst was carried out by Du *et al.* (2007). At 873 K, 1 wt% of Ni-MCM-41 with space velocity of 115001 $kg^{-1}h^{-1}$ showed

only 46.5% CO_2 conversion and a selectivity of 39.6% towards CH_4. Almost no catalytic activity was detected at 373-473 K and only negligible amounts of products were detected at 573 K. However, this catalyst structure did not change much after CO_2 methanation for several hours, producing the high physical stability of this catalytic system.

In addition, nickel based catalysts that used more than one dopants had been studied by Liu *et al.* (2009). Ni-Ru-B/ZrO_2 catalyst was prepared by means of chemical reduction and dried at 80°C for 18 h in air with total gas flow rate of 100 cm^3/min. They found that CO_2 methanation occurred only when temperature was higher than 210°C. At reaction temperature of 230°C, the CO conversion reached 99.93% but CO_2 conversion only 1.55%. Meanwhile, Ni-Fe-Al oxide nano-composites catalyst prepared by the solution-spray plasma technique for the high temperature water-gas shift reaction was investigated by Watanabe *et al.* (2009). The CO conversion over 39 atom% Ni-34 atom% Fe-27 atom% Al catalyst achieved around 58% and yielded about 6% of methane at 673 K.

On the other hand, Kodama *et al.* (1997) had synthesized ultrafine $Ni_xFe_{3-x}O_4$ with a high reactivity for CO_2 methanation by the hydrolysis of Ni^{2+}, Fe^{2+} and Fe^{3+} ions at 60-90°C followed by heating of the co-precipitates to 300°C. At reaction temperature of 300°C, the maximum yield (40%) and selectivity (95%) for CH_4 were obtained. Moreover, the conversion of CO_2 over NiO-YSZ-CeO_2 catalyst prepared by impregnation method was 100% at temperature above 800°C. This catalyst was investigated by Kang *et al.* (2007). No NiC phase was detected on the surface of NiO-YSZ-CeO_2 catalyst. Yamasaki *et al.* (1999) reported that amorphous alloy of Ni-25Zr-5Sm catalyzed the methanation reaction with 90% conversion of CO_2 and 100% selectivity towards CH_4 at 300°C.

Furthermore, Ocampo *et al.* (2009) had investigated the methanation of carbon dioxide over 5 wt% nickel based $Ce_{0.72}Zr_{0.28}O_2$ catalyst which prepared by pseudo sol-gel method. The catalyst exhibited high catalytic activity with 71.5% CO_2 conversion and achieved 98.5% selectivity towards methane gas at 350°C. However, it never stabilized and slowly deactivated with a constant slope and ended up with 41.1% CO_2 conversion and its CH_4 selectivity dropped to 94.7% after 150 h on stream. Catalytic testing was performed under operating conditions at pressure of 1 atm and a $CO_2/H_2/N_2$ ratio is 36/9/10 with a total gas flow of 55 mL/min.

Meanwhile, Kramer *et al.* (2009) also synthesize $Re_2Zr_{10}Ni_{88}O_x$ catalyst by modified sol gel method based on the molar ratio metal then dried for 5 days at room temperature followed by 2 days at 40°C and lastly calcined at 350°C for 5 h. The catalytic performance was carried out by the reactant gas mixture of $CO/CO_2/N_2/H_2$ = 2/14.9/19.8/63.3 enriched with water at room temperature under pressure of 1 bar and total flow rate of 125 mL/min. At reaction temperature of 230°C, almost 95% conversion of CO was occurred and less than 5% for conversion of CO_2 over this catalyst.

The novel catalyst development to achieve both low temperature and high conversion of sour gasses of H_2S and CO_2 present in the natural gas was investigated by Wan Abu Bakar *et al.* (2008c). It was claimed that conversion of H_2S to elemental sulfur achieved 100% and methanation of CO_2 in the presence of H_2S yielded 2.9% of CH_4 over Fe/Co/Ni-Al_2O_3 catalyst at maximum studied temperature of 300°C. This exothermic reaction will generate a significant amount of heat which caused sintering effect towards the catalysts (Hwang and Smith, 2009). Moreover, exothermic reaction is unfavorable at low temperature due to its low energy content. Thus, the improvement of catalysts is needed for the in-situ reactions of methanation and desulfurization to be occurred at lower reaction temperature.

4.2 Manganese Based used in Methanation Catalysts

Manganese has been widely used as a catalyst for many types of reactions including solid state chemistry, biotechnology, organic reactions and environmental management. Due to its properties, numerous field of research has been investigated whereby manganese is employed as the reaction catalyst. Although nickel also reported to be applicable in many process as a good and cheap catalysts, it seems that using nickel as based catalysts will deactivated the active site by deposition of carbon (Luna *et al.,* 2008). Hence, it is essential to use other metal to improve the activity and selectivity as well as to reduce formation of carbon. A proof that manganese improves the stability of catalysts can be shown in researched done by Seok. H. S *et al* (2001). He have proven that manganese improve the stability of the catalyst in CO_2 reforming methane. Added Mn to Ni/Al_2O_3 will promotes adsorption CO_2 by forming carbonate species and it was responsible for suppression of carbon deposition over $Ni/MnO\text{-}Ni/Al_2O_3$. Other research done by Li. J *et al.* (2009) prove that when manganese doped in appropriate amount, it will cause disorder in the spinal structure of metal surface and can enhance the catalytic activity of the reactive ion.

According to Ouaguenouni *et al,* [33], in the development of manganese oxide doped with nickel catalyst, they found that the spinel $NiMn_2O_4$ was active in the reaction of the partial oxidation of methane. The catalysts show higher methane conversion when calcined at 900°C. This is because the stability of the structure which led to good dispersion of nickel species. Indeed, the presence of the oxidized nickel limited the growth of the particles probably by the formation of interaction between metallic nickel out of the structure and the nickel oxide of the structure.

Ching [34] in his studies found that, 5% of manganese that had been introduced into cobalt containing nickel oxide supported alumina catalyst will converted only 17.71% of CO_2 at reaction temperature of 300°C. While when Mn was introduced into iron containing nickel oxide supported alumina catalyst, the percentage of CO_2 conversion does not differ much as in the Co:Ni catalyst. This may be because manganese is not a good dopant for nickel based catalyst. This is in agreement by Wachs *et al.* [35], where some active basic metal oxide components such as MnO and CeO did not interact strongly with the different oxide functionalities present on oxide support and consequently, did not disperse very well to form crystalline phases. Therefore, in research done by Wachs *et al.* [36] stated that Ru could be assigned as a good dopant towards MnO based catalyst. They are active basic metal oxides that usually anchor to the oxide substrate by preferentially titrating the surface Lewis acid sites, such as surface M-oxide vacancies, of the oxide support.

In addition, the hydrogenation of carbon oxides was also performed over promoted iron-manganese catalysts. Herranz *et al.* [37] in their research found that manganese containing catalyst showed higher activity towards formation of hydrocarbons. When these catalysts were promoted with copper, sodium and potassium, carbon dioxide conversion was favoured by alkaline addition, especially by potassium, due to the promotion of the water-gas shift reaction.

When Najwa Sulaiman (2010) incorporated ruthenium into the manganese oxide based catalyst system with the ratio of 30:70 that was $Ru/Mn\ (30:70)/Al_2O_3$, it gave a positive effect on the methanation reaction. The percentage conversion keeps on increasing at 200°C with a percentage of CO_2 conversion of 17.18% until it reaches its maximum point at 400°C, whereby the percentage of CO_2 conversion is at the highest which is 89.01%. At reaction temperature of 200°C and 400°C, it showed Mn and Ru enhances the catalytic activity

because H_2 and CO_2 are easily chemisorbed and activated on these surfaces. Murata *et al.* (2009) suggested that the high CO_2 conversion was probably due to the manganese species which causes the removal of chlorine atoms from $RuCl_3$ precursor and increases the density of active ruthenium oxide species on the catalyst which resulted in high catalytic activity.
Furthermore, it is very important to used stable and effective metal oxide catalyst with improved resistance to deactivation caused by coking and poisoning. Baylet. A *et al.* (2008) studies on effect of Pd on the reducibility of Mn based material. They found that in H_2-TPR and XPS test, only Mn^{3+}/Mn^{2+} is proportional to the total Mn content in the solid support that leads to the stable catalyst to avoid cooking and poisoning effect. Additionally, Hu. J *et al*. (2008) in their research on Mn/Al_2O_3 calcined at 500°C, shows that manganese oxide proved to have a good performance for catalytic oxidation reaction and also show better catalytic performance compare using support SiO_2 and TiO_2. It is shows that not only doped material are important in producing good catalyst, based catalyst also play major role in giving high catalytic activity in catalysts. El-Shobaky *et al.* (2003) studied, the doping process did not change the activation energy of the catalyzed reaction but much increased the concentration of the catalytically reactive constituents without changing their energetic nature.
Other research made by Chen. H. Y *et al* (1998) revealed the important of promoting manganese in catalyst. The studies shows that when $Cu/ZnO/Al_2O_3$ promoted Mn as based catalyst, it shows increasing in catalytic activity, larger surface area of Cu concentration and elevated Cu reduction temperature compare catalyst without Mn. In XPS studies also revealed that reaction between Mn and Cu resulting reduction of Mn^{4+} to Mn^{3+} as well as oxidation of Cu^0 and Cu^+ to higher oxidation state. The most important result is, added Mn enhanced methanation yield up to 5-10%. This is an agreement with Wojciechowska. M *et al.* (2007) where in they found that when using manganese as based in copper catalyst increase methane yield and activated the catalyst more compare to copper-cooper catalyst.
Wachs *et al.* (2005) found that some active basic metal oxide components such as MnO and CeO did not interact strongly with the different oxide functionalities present on oxide support and consequently, did not disperse very well to form crystalline phases. Therefore, in research done by Wachs *et al*. (1996) stated that Ru could be assigned as a good dopant towards MnO based catalyst. They are active basic metal oxides that usually anchor to the oxide substrate by preferentially titrating the surface Lewis acid sites, such as surface M-oxide vacancies, of the oxide support.

4.3 Noble Metals used in Methanation Catalysts

Nickel oxide will lose its catalytic ability after a few hours when it undergoes carbon formation process. The carbon formation can be avoided by adding dopants towards the Ni catalyst. Therefore, incorporating of noble metals will overcome this problem. Noble metals such as rhodium, ruthenium, platinum and iridium exhibit promising CO_2/H_2 methanation performance, high stability and less sensitive to coke deposition. However, from a practical point of view, noble metals are expensive and little available. In this way, the addition of dopants and support is good alternative to avoid the high cost of this precious metal. For the same metal loading, activity is mainly governed by the type of metal but also depends on precursor selection (Yaccato *et al.,* 2005). While, the reaction selectivity depends on support type and addition of modifier (Kusmierz, 2008).

Methane production rates for noble metals based catalysts were found to decrease in order Ru > Rh > Pt > Ir ~ Pd. It may be suggested that the high selectivities to CH_4 of Ru and Rh are attributed to the rapid hydrogenation of the intermediate CO, resulting in higher CO_2 methanation activities. Panagiotopoulou *et al.* (2008) had claimed the selectivity towards methane which typically higher than 70%, increases with increasing temperature and approaches 100% when CO_2 conversion initiated at above 250°C. A different ranking of noble metals is observed with respect to their activity for CO_2 hydrogenation, where at 350°C decreases by about one order of magnitude in the order of Pt > Ru > Pd ~ Rh. From the research of Ali *et al.* (2000), the rate of hydrogenation can be increased by loading noble metals such as palladium, ruthenium and rhodium. The results showed that all of them perform excellently in the process of selective oxidation of CO, achieving more than 90% conversion in most of the temperature region tested between 200°C to 300°C.

Finch and Ripley (1976) claimed that the noble metal promoters may enhance the activity of the cobalt supported catalysts to increase the conversion to methane. In addition, the noble metals promoted catalysts maintained greater activity for methane conversion than the non-promoted catalysts in the presence of sulfur poison. The addition of small contents of noble metals on cobalt oxides has been proposed in order to increase the reduction degree on the catalytic activity of Co catalysts (Profeti *et al.*, 2007). Research done by Miyata *et al.* (2006) revealed that the addition of Rh, Pd and Pt noble metals drastically improved the behavior of Ni/Mg(Al)O catalysts. The addition of noble metals on Ni resulted in a decrease in the reduction temperature of Ni and an increase in the amount of H_2 uptake on Ni on the catalyst.

It well known that ruthenium is the most active methanation catalyst and highly selective towards methane where the main products of the reaction were CH_4 and water. However, the trace amount of CO was present among the products and methanol was completely absent (Kusmierz, 2008). Takeishi and Aika (1995) who had studied on Raney Ru catalysts found a small amount of methanol was produced on supported Ru catalyst but the methane gas was produced thousands of times more than the amount of methanol from CO_2 hydrogenation. The selectivity to methane was 96-97% from CO_2. Methane production rate from CO_2 and H_2 at 500 K on their Raney Ru was estimated to be 0.25 mol g^{-1} h^{-1}. The activity for methane production from CO_2 ± H_2 at 433 K under 1.1 MPa was much higher than that under atmospheric pressure. The rate of methane synthesis was 3.0 mmol g^{-1} h^{-1} and the selectivity for methane formation was 98% at 353 K, suggesting the practical use of this catalyst (Takeish *et al.*, 1998).

Particularly suitable for the methanation of carbon dioxide are Ru/TiO_2 catalysts. Such catalysts display their maximum activity at relatively low temperatures which is favorable with respect to the equilibrium conversion of the strongly exothermic reaction and form small amount of methane even at room temperature (Traa and Weitkamp, 1999). It can be prove by VanderWiel *et al.* (2000) who had studied on the production of methane from CO_2 via Sabatier reaction. The conversion reaches nearly 85% over 3 wt% Ru/TiO_2 catalyst at 250°C and the selectivity towards methane for this catalyst was 100%.

Meanwhile, a microchannel reactor has been designed and demonstrated by Brooks *et al.* (2007) to implement the Sabatier process for CO_2 reduction of H_2, producing H_2O and CH_4. From the catalyst prepared, the powder form of Ru/TiO_2 catalyst is found to provide good performance and stability which is in agreement with Abe *et al.* (2008). They claimed that the CO_2 methanation reaction on Ru/TiO_2 prepared by barrel-sputtering method produced a

100% yield of CH_4 at 160°C which was significantly higher than that required in the case of Ru/TiO_2 synthesize by wetness impregnation method and Gratzel method. Barrel-sputtering method gives highly dispersed Ru nano particles deposited on the TiO_2 support which then strongly increase its methanation activity.

Another research regarding CO-selective methanation over Ru-based catalyst was done by Galletti *et al.* (2009). The γ-Al_2O_3 to be used as Ru carrier was on purpose prepared through the solution combustion synthesis (SCS) method. The active element Ru was added via the incipient wetness impregnation (IWI) technique by using $RuCl_3$ as precursor. Three Ru loads were prepared: 3%, 4% and 5% by weight. All of the catalysts reached complete CO conversion in different temperature ranges where simultaneously both the CO_2 methanation was kept at a low level and the reverse water gas shift reaction was negligible. The best results were obtained with 4% Ru/γ-Al_2O_3 in the range of 300–340°C, which is 97.40% of CO conversion.

For further understanding about methanation over Ru-based catalysts, Dangle *et al.* (2007) conducted a research of selective CO methanation catalysts prepared by a conventional impregnation method for fuel processing applications. It well known that metal loading and crystallite size have an affect towards the catalyst activity and selectivity. Therefore, they was studied the crystallite size by altering metal loading, catalyst preparation method, and catalyst pretreatment conditions to suppress CO_2 methanation. These carefully controlled conditions result in a highly active and selective CO methanation catalyst that can achieve very low CO concentrations while keeping hydrogen consumption relatively low. Even operating at a gas hourly space velocity as high as 13500 h^{-1}, a 3% Ru/Al_2O_3 catalyst with a 34.2 nm crystallite was shown to be capable of converting 25–78% of CO_2 to CH_4 over a wide temperature range from 240 to 280°C, while keeping hydrogen consumption below 10%.

In addition, Gorke and Co-workers (2005) had carried out research on the microchannel reactor which coated with a Ru/SiO_2 and a Ru/Al_2O_3 catalyst. They found that the Ru/SiO_2 catalyst exhibits its highest CH_4 selectivity of only 82% with 90% CO_2 conversion at a temperature of 305°C, whereas a selectivity of 99% is obtained by the Ru/Al_2O_3 catalyst at 340°C with CO_2 conversion of 78%. However, Weatherbee and Bartholomew (1984) achieved a CH_4 selectivity of 99.8% with CO_2 conversion of only 5.7% at reaction temperature of 230°C using Ru/SiO_2 catalyst.

Mori *et al.* (1996) investigated the effect of reaction temperature on CH_4 yield using Ru-MgO under mixing and miling conditions at initial pressures of 100 Torr CO_2 and 500 Torr H_2. No CH_4 formation was observed at the temperatures below 80°C under mixing conditions over Ru-MgO catalyst. It reached 31% at 130°C but leveled off at 180°C. CH_4 formation over this catalyst under milling condition increased from 11% at 80°C to 96% at 180°C. They found that incorporating of MgO, a basic oxide to the Ru, promotes the catalytic activity by strongly adsorbing an acidic gas of CO_2. According to Chen *et al.* (2007), Ru impregnated on alumina and modified with metal oxide (K_2O and La_2O_3) showed that the activity temperature was lowered approximately 30°C compared with pure Ru supported on alumina. The conversion of CO on Ru-K_2O/Al_2O_3 and Ru-La_2O_3/Al_2O_3 was above 99% at 140–160°C, suitable to remove CO in a hydrogen-rich gas and the selectivity of Ru-La_2O_3/Al_2O_3 was higher than that of Ru-K_2O/Al_2O_3 in the active temperature range. While methanation reaction was observed at temperature above 200°C.

Other than that, Szailer *et al.* (2007) had studied the methanation of CO_2 on noble metal supported on TiO_2 and CeO_2 catalysts in the presence of H_2S at temperature 548 K. It was

observed that in the reaction gas mixture containing 22 ppm H_2S, the reaction rate increased on TiO_2 and on CeO_2 supported metals (Ru, Rh, Pd) but when the H_2S content up to 116 ppm, the all supported catalysts was poisoned. In the absence of H_2S, the result showed that 27% conversion of CO_2 and 39% conversion of CO_2 to methane with the presence of 22 ppm H_2S after 4 hours of the reaction.

Moreover, the addition of Rh strongly improves the activity and stability of the catalysts (Wu and Chou, 2009), resistance to deactivation and carbon formation can be significantly reduced (Jozwiak *et al.*, 2005). Erdohelyi *et al*. (2004) studied the hydrogenation of CO_2 on Rh/TiO_2. The rate of methane formation was unexpectedly higher in the $CO_2 + H_2$ reaction on Rh/TiO_2 in the presence of H_2S. At higher temperature of 673 K, around 75% of selectivity for CH_4 formation and CO was also formed from the reaction. Choudhury *et al*. (2006) presented the result of an Rh-modified $Ni\text{-}La_2O_3\text{-}Ru$ catalyst for the selective methanation of CO. However, the performance of the prepared catalysts was reported to be that CO_2 conversion appeared to be less than 30% when CO converted completely.

It had been reported that the addition of Pd had a positive effect for hydrogenation of CO or CO_2 because of its higher electronegativity with greater stability of Pd^0 species compared to those of Ni^0 under on stream conditions (Castaño *et al.*, 2007). In contrast, Pd/SiO_2 and Pt/SiO_2 catalysts showed poor activities at temperature lower than 700 K with the CO conversion was not greater than 22% at temperature 823 K over these catalysts (Takenaka *et al.*, 2004). A $Pd–Mg/SiO_2$ catalyst synthesized from a reverse microemulsion has been found to be active and selective for CO_2 methanation (Park *et al.*, 2009). At 450°C, the $Pd\text{-}Mg/SiO_2$ catalyst had greater than 95% selectivity to CH_4 at a carbon dioxide conversion of 59%. They claimed that the similar catalyst without Mg has an activity only for CO_2 reduction to CO. these results support a synergistic effect between the Pd and Mg/Si oxide.

Furthermore, platinum-based catalysts present an activity and a selectivity that are almost satisfactory. Finch and Ripley (1976) claimed that the tungsten-nickel-platinum catalyst was substantially more active as well as sulfur resistant than the catalyst in the absence of platinum. It was capable to show a conversion of 84% of CO after on stream for 30 minutes in the presence of less than 0.03% CS_2. No catalytic activity was observed under the poison of 0.03% CS_2 without the addition of Pt. The platinum group promoters enabled the catalysts to maintain good activity until the critical concentration of poison was reached. Pt catalysts were most well known as effective desulfurizing catalysts. Panagiotopolou and Kodarides (2007) found that the platinum catalyst is inactive in the temperature range of 200°C-400°C, since temperatures higher than 450°C are required in order to achieve conversion above 20%.

Moreover, Nishida *et al.* (2008) found that the addition of 0.5 wt% Pt towards *cp*-Cu/Zn/Al (45/45/10) catalyst was the most effective for improving both activity and sustainability of the catalyst. At 250°C, the conversion of CO was achieved around 77.1% under gas mixture of $CO/H_2O/H_2/CO_2/N_2$ = 0.77/2.2/4.46/0.57/30 mL/min. Pierre *et al* (2007) found that the conversion of CO over 5.3% PtCeOx catalyst prepared by urea gelation co-precipitation (UGC) which was calcined at 400°C reached about 92%. This catalyst is more active and shows excellent activity and stability with time on stream at 300°C under water gas shift reaction.

Recently, Bi *et al.* (2009) found that $Pt/Ce_{0.6}Zr_{0.4}O_2$ catalyst exhibited a markedly higher activity with 90.4% CO conversion at 623 K for the water gas shift (WGS) reaction. The methane selectivity was only 0.9% over this catalyst which has been prepared by wetness

impregnation method. Meanwhile, Utaka *et al.* (2003) examined the reaction of a simulated reforming gas over Pt-catalysts. At temperatures from 100°C to 250°C, high CO conversions of more than 90% were obtained but most of the conversion was caused by water gas shift reaction. The use of platinum catalyst in conversion of cyclohexane was conducted by Songrui et al. (2006). They found that the cyclohexane conversion over Pt/Ni catalyst prepared by impregnation method (55%-53%) was obviously higher than that over Pt/Al_2O_3 catalyst (30%-20%).

4.4 Supports for the Methanation Catalysts

The presence of the support was recognized to play an important role since it may influence both the activity and selectivity of the reaction as well as control the particle morphology. Insulating oxides such as SiO_2, y-Al_2O_3, V_2O_5, TiO_2 and various zeolites usually used as material supports. These supports are used to support the fine dispersion of metal crystallites, therefore preparing them to be available for the reactions. These oxides will possess large surface area, numerous acidic/basic sites and metal-support interaction that offer particular catalytic activity for many reactions (Wu and Chou, 2009).

Alumina is often used as support for nickel catalyst due to its high resistance to attrition in the continuously stirred tank reactor or slurry bubble column reactor and its favorable ability to stabilize a small cluster size (Xu *et al.*, 2005). Alumina does not exhibit methanation activity, it was found to be active for CO_2 adsorption and the reverse spillover from alumina to nickel increases the methane production especially for co-precipitated catalyst with low nickel loading (Chen and Ren, 1997). Happel and Hnatow (1981) also said that alumina could increase the methanation activity although there was presence of low concentration of H_2S. Additionally, Chang *et al.* (2003) believed that Al_2O_3 is a good support to promote the nickel catalyst activity for CO_2 methanation by modifying the surface properties. Supported Ni based catalyst in the powder form usually used by many researchers and only few researchers used a solid support for their study.

Mori *et al.* (1998) had studied the effect of nickel oxide catalyst on the various supports material prepared using impregnation technique. They revealed that the reactivity of the catalysts depended on the type of supports used which follow the order of Al_2O_3 > SiO_2 > TiO_2 > $SiO_2{\cdot}Al_2O_3$. The reason for the higher activity of Ni/Al_2O_3 catalyst with 70% methanation of CO_2 at 500°C was attributed to the basic properties of the Al_2O_3 support on which CO_2 could be strongly adsorbed and kept on the catalyst even at higher temperatures. However, Takenaka *et al.* (2004) found that the conversion of CO at 523 K were higher in the order of Ni/MgO (0%) < Ni/Al_2O_3 (7.9%) < Ni/SiO_2 (30.0%) < Ni/TiO_2 (42.0%) < Ni/ZrO_2 (71.0%). These results implied that Al_2O_3 support was not appropriate for the CO conversion but suitable support for CO_2 conversion.

In addition, Seok *et al.* (2002) also prepared various Ni-based catalysts for the carbon dioxide reforming of methane in order to examine the effects of supports (Al_2O_3, ZrO_2, CeO_2, La_2O_3 and MnO) and preparation methods (co-precipitated and impregnated) on the catalytic activity and stability. Catalytic activity and stability were tested at 923 K with a feed gas ratio CH_4/CO_2 of 1 without a diluent gas. Co-precipitated Ni/Al_2O_3, Ni/ZrO_2, and Ni/CeO_2 showed high initial activities but reactor plugging occurred due to the formation of large amounts of coke. The gradual decrease in the activity was observed for Ni/La_2O_3 and Ni/MnO, in which smaller amounts of coke were formed than in Ni/Al_2O_3, Ni/ZrO_2, and Ni/CeO_2. The catalyst deactivation due to coke formation also occurred for

impregnated 5 wt% Ni/γ-Al_2O_3 catalysts. Addition of MnO onto this Ni/γ -Al_2O_3 catalyst decreased the amount of deposited coke drastically and 90% of initial CO_2 conversion was maintained after 25 h.

Zhou *et al.* (2005) had synthesized the Co-Ni catalyst support with activated carbon for CO selective catalytic oxidation. The conversion of Co-Ni/AC catalyst always keeps at above 97% in a wide reaction temperature of 120-160^{o}C. However, the CO conversion dramatically decreases with the increasing temperature when the reaction temperature is beyond 160^{o}C. Activated carbons are used efficiently in many environmental remediation processes due to their high adsorption capacity, which makes their use possible in the removal of great variety of pollutants present in air aqueous medium. This is because, besides their high surface area, they possess several functional surface groups with an affinity for several adsorbates, justifying the extreme relevance of this adsorbent for the treatment of the pollutant (Avelar *et al.*, 2010).

Kowalczky *et al*. (2008) had revealed that the reactions of trace CO_2 amount with hydrogen (low CO_x /H_2 ratios) are dependent on the Ru dispersion and the kind of support for the metal. Among the supports used in the present study (low and high surface area graphitized carbons, magnesia, alumina and a magnesium–aluminum spinel), alumina was found to be the most advantageous material. For similar Ru dispersions, CO methanation over Ru/Al_2O_3 at 220^{o}C was about 25 times and CO_2 methanation was about 8 times as high as ruthenium deposited on carbon B (Ru3/CB). For high metal dispersion, the following of sequence was obtained: Ru/Al_2O_3 > Ru/$MgAl_2O_3$ > Ru/MgO > Ru/C, both for CO and CO_2 methanation. It is suggested that the catalytic properties of very small ruthenium particles are strongly affected by metal–support interactions. In the case of Ru/C systems, the carbon support partly covers the metal surface, thus lowering the number of active sites (site blocking).

Takenaka *et al.* (2004) also found that at 473 K, Ru/TiO_2 catalyst showed the highest activity among all the catalysts but when the reaction temperature increased to 523 K, the CO conversion was follows the order of Ru/MgO (0%) < Ru/Al_2O_3 (62.0%) < Ru/SiO_2 (85.0%) < Ru/ZrO_2 (100.0%) = Ru/TiO_2 (100.0%). Similarly to Görke *et al.* (2005) who found that Ru/SiO_2 catalysts exhibits higher CO conversion and selectivity, compared to Ru/Al_2O_3. Meanwhile, Panagiotopolou and Kodarides (2007) demonstrated that Pt/TiO_2 is the most active catalyst at low temperatures exhibiting measurable CO conversion at temperature as low as 150^{o}C. Conversion of CO over this catalyst increases with increasing temperature and reach 100% at temperature of 380^{o}C. While, platinum catalyst supported on Nd_2O_3, La_2O_3 and CeO_2 become active at temperature higher than 200^{o}C and reach 100% above 400^{o}C. MgO and SiO_2 supported platinum catalysts are practically inactive in the temperature range of interest.

The detailed studied on the SiO_2 and Al_2O_3 support was investigated by Nurunnabi *et al.* (2008) had investigated the performance of γ-Al_2O_3, α-Al_2O_3 and SiO_2 supported Ru catalysts prepared using conventional impregnation method. They found that γ-Al_2O_3 support is more effective than catalysts α-Al_2O_3 and SiO_2 supports for Fischer-Tropsch synthesis under reaction condition of P=20 bar, H_2/CO=2 and GHSV=1800/h. γ-Al_2O_3 showed a moderate pore and particle size around 8 nm which achieved higher catalytic activity about 82.6% with 3% methane selectivity than those of α-Al_2O_3 and SiO_2 catalysts. Pentasil-type zeolite also could be used as a support for the catalysts which exhibited high

activity and stability due to not only the basicity of alkaline promoters but also the incorporation with zeolite support (Park *et al*., 1995).
Furthermore, Solymosi *et al.* (1981) reported a sequence of activity of supported rhodium catalysts of Rh/TiO_2 > Rh/Al_2O_3 > Rh/SiO_2. This order of CO_2 methanation activity and selectivity was the same as observed for Ni on the same support by Vance and Bartheolomew *et al.* (1983). These phenomena can be attributed to the different metal-support electronic interactions which affects the bonding and the reactivity of the chemisorbed species.

5. Conclusion

Natural gas fuel is a green fuel and becoming very demanding because it is environmental safe and clean. Furthermore, this fuel emits lower levels of potentially harmful by-products into the atmosphere. Most of the explored crude natural gas is of sour gas and yet, very viable and cost effective technology is still need to be developed. Above all, methanation technology is considered a future potential treatment method for converting the sour natural gas to sweet natural gas.

6. References

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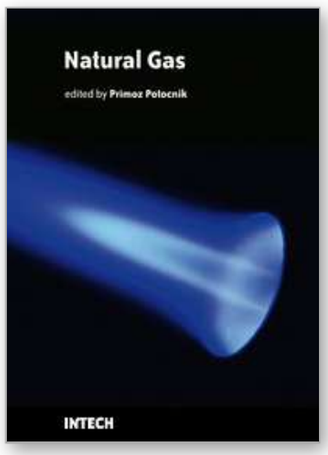

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The contributions in this book present an overview of cutting edge research on natural gas which is a vital component of world's supply of energy. Natural gas is a combustible mixture of hydrocarbon gases, primarily methane but also heavier gaseous hydrocarbons such as ethane, propane and butane. Unlike other fossil fuels, natural gas is clean burning and emits lower levels of potentially harmful by-products into the air. Therefore, it is considered as one of the cleanest, safest, and most useful of all energy sources applied in variety of residential, commercial and industrial fields. The book is organized in 25 chapters that cover various aspects of natural gas research: technology, applications, forecasting, numerical simulations, transport and risk assessment.

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